

CAN RE-USE OF DEMIL EXPLOSIVES AND PROPELLANTS IN COMMERCIAL BLASTING BE MADE ENVIRONMENTALLY ACCEPTABLE?

Per-Anders Persson, Research Center for Energetic Materials
New Mexico Institute of Mining and Technology, Socorro, NM 87801

ABSTRACT

Some modern commercial blasting agents such as ANFO are of an oxygen balanced composition, i.e. their composition is such that there is just enough oxygen (mostly from ammonium nitrate) to oxidize all the hydrogen in the composition to water, all the carbon to carbon dioxide, and any aluminum to alumina, Al_2O_3 . Such blasting agents in ideal detonation give a minimum of polluting and toxic reaction product gases, such as CO, NO, NO_2 , NH_3 , and CH_4 , to mention a few. When blasting agents are used in large (6 - 13 inch diameter) drillholes in blasting with heavy overburdens of rock, there is generally enough time for the chemical reactions to reach equilibrium while the pressure is still high. This results in a very complete and clean combustion, closely resembling that of an ideal detonation. A condition for clean burn is that the fuel and oxidizing ingredients are intimately mixed.

Many commercial emulsion and slurry explosives are not oxygen balanced - most contain more fuel in the form of hydrocarbon oils, fuel oil, mineral oil, and emulsifiers, which are also hydrocarbons. When the composition is not oxygen balanced, either positive or negative (an explosive with a positive oxygen balance has more oxygen, one with a negative oxygen balance has less oxygen than the oxygen balanced composition), then the production of toxic and polluting gases increases rapidly. When explosives with a positive oxygen balance detonate, large quantities of NO and NO_2 are formed; when explosives with a negative oxygen balance detonate, large quantities of CO, H_2 , NH_3 , CH_4 , and other gases are formed, the larger quantities the larger the deviation is from oxygen balance.

Present methods for re-using propellants often rely on simply adding the demil material (a military explosive in the form of flakes, smokeless propellant grains of different sizes, or large or small pieces of AP/Al base solid rocket propellants) to a standard emulsion or slurry blasting agent. These added components by themselves all have a negative oxygen balance: TNT and Comp. B have large negative oxygen balances, AP/Al-based booster rocket propellants have moderate negative balances, and smokeless powders have small negative oxygen balances. When present in large pieces, these materials produce reaction products which appear not to mix and burn completely in the surrounding commercial explosive's reaction products. Consequently, the demil materials do not burn cleanly, even in large diameter drillholes in rock, and the production of toxic and polluting gases from the demil material may be equal to or even greater than that from open detonation of that material by itself.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE AUG 1994		2. REPORT TYPE		3. DATES COVERED 00-00-1994 to 00-00-1994	
4. TITLE AND SUBTITLE Can Re-Use of Demil Explosives and Propellants in Commercial Blasting Be Made Environmentally Acceptable?				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Research Center for Energetic Materials, New Mexico Institute of Mining and Technology, Socorro, NM, 87801				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM000767. Proceedings of the Twenty-Sixth DoD Explosives Safety Seminar Held in Miami, FL on 16-18 August 1994.					
14. ABSTRACT see report					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 14	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

This paper illustrates these points with computer calculations of the reaction product composition from proposed explosives with and without demil additions, and from demil materials detonated by themselves. A few oxygen balanced blasting agents comprising demil explosives and propellants are suggested, which can be shown will produce clean reaction products. A program of verification of the findings is proposed.

1. BACKGROUND

Very large quantities of explosives and propellants at present in the U.S. military inventory are expected to be released for demilitarization within the next few years. According to one source, the quantity of stockpiled munitions to be demilitarized in the U.S. is 340,000 short tons, increasing annually by at least 20,000 tons. Much of this mass is steel, such as in artillery projectiles and bomb casings, but 15 to 20 percent, (50,000 to 70,000 tons) is high explosives and another 10 percent is propellants. Even larger quantities are waiting to be demilitarized in the republics of the former Soviet Union, particularly in Russia and in the Ukraine. The demil energetic materials available in the largest quantities are smokeless powder propellants from artillery ammunition, TNT from artillery shells, and composite large rocket propellants with ammonium perchlorate, aluminum, and a plastic binder as the main ingredients. Smaller quantities of Tritonal and other aluminized explosives from underwater mines are also waiting to be demilitarized. To put the quantities of demil energetic materials in perspective, during the recent Iraq-Kuwait conflict, the total weight of air bombs delivered in one day was about 10,000 tons.

Seen from another perspective, the quantities of energetic materials to be demilitarized are not overwhelmingly large. The U.S. commercial explosives consumption for mining and minerals recovery in 1991 was about 2,000,000 short tons. The quantity of commercial explosives used annually in Russia alone is probably almost as large. Crudely put, less than a month's rock blasting in the U.S. and Russia would consume all of the high explosives and propellants in the surplus munitions stockpile of both countries, if it could be used for that purpose.

If the surplus materials could be recycled into commercial explosives and blasting agents, they would become an asset rather than a problem. However, the stockpile consists of a variety of munitions containing many different explosives and propellants, not all of which can be safely recycled in this way. Developments are underway to destroy these materials in environmentally acceptable ways. The methods considered are open burning or detonation, incineration, and supercritical water oxidation. Overall, the U.S. Army, as the single service manager for the ammunition production base and stockpile has by far the largest quantity of explosives for disposal in the U.S. About 95 % of the current destruction of explosives is done by open burning or detonation; it is hoped that this figure can be reduced to 5 % by the introduction of other destruction methods or by re-cycling or re-use of the materials.

The Army is at present allowed to burn or detonate explosives in the open air only until 1995. Currently, the use of such techniques as chemical destruction by supercritical water oxidation is only considered for the destruction of colored smokes and similar pyrotechnics that yield carcinogenic decomposition products.

Very little of the explosives material is in bulk form; most of it is in munitions that currently must be down-loaded before the bulk material is available. When down-loaded, the explosives materials as a rule no longer meet the military specifications for re-use for its original purpose in new munitions, although some of them, such as TNT, may well be relatively easily re-processed to meet specifications. However, it appears likely that the demand for new munitions for the foreseeable future will be much less than the volume of material that must be demilitarized because of lack of storage space.

Down-loading of explosives from munitions costs about \$3000 per 2000 lbs; open burning a further \$800 - \$1800 per short ton and chemical destruction \$200 - \$1000 per ton, the latter without consideration of the disposal of residual waste liquids generated in the process. Downloading obviously is going to be a major industrial undertaking, considering the quantities mentioned above. Clearly, if there are commercial uses for the explosives, the tax payer could stand to benefit greatly, and possibly also the buyer or user of such products.

2. MODERN COMMERCIAL EXPLOSIVES

To evaluate the economics, safety aspects, and environmental impact of using demil explosives and propellants in commercial rock blasting, it is necessary to have a basic understanding of the purpose of the blasting operation, the standard products currently used, and their prices. All rock blasting operations depend on the detonation of columns of explosives placed in holes drilled in the rock mass to be fragmented. A large blast may contain hundreds of drillholes each containing up to a ton of explosive. The following is a short summary of the major groups of commercial explosives used at present or in the past.

Dynamite

Dynamite, a mix of ammonium nitrate with nitroglycerine and/or nitroglycol and other ingredients, is used only in very small quantities today, mainly for special applications under difficult conditions in underground or small-scale blasting above ground.

ANFO

By far the largest volume product in commercial rock blasting today is ANFO (Ammonium Nitrate/Fuel Oil), consisting of 1 - 3 mm diameter slightly porous granules (prills) of ammonium nitrate, mixed with about 6 % fuel oil, which is absorbed in the pores, making the bulk material free-flowing, so that it can be augered from a bulk container into drillholes with diameters ranging from 4 to 15 inch. About 85 % of the 2,000,000 short tons of commercial explosives used in the U.S. is ANFO, and a major part of the ANFO is mixed on site by adding fuel oil to the auger moving the AN prills from the truck to the drillhole. The current (June 1994) price of AN prills in large bulk quantities is about \$150 per short ton, the price of ANFO delivered into the drillhole in bulk varies from \$170 - \$180 per ton.

Emulsion Explosives and Blasting Agents

Another large volume product group comprises the *emulsion explosives* or *emulsion blasting agents*, essentially consisting of a supercooled concentrated solution of AN in water, emulsified into a mix of fuel oil and emulsifier. Typical order of magnitude weight

percentages of the main ingredients in an emulsion blasting agent are 75 % AN, 17 % water, and 8 % fuel oil/emulsifier. The bulk emulsion has a consistency similar to that of sandwich spread mayonnaise, and it contains small gas bubbles or hollow glass microballoons which serve as shock initiation hot spots to make the otherwise very insensitive material able to detonate. The oil/emulsifier is the outer phase of the emulsion, so that the water soluble ammonium nitrate-containing inner phase is shielded from contact with water. The emulsion is therefore water repellent, somewhat like a goose. The price of bulk emulsion blasting agents in large quantity is from \$200 to \$225 per short ton or more, higher the higher the content of glass microballoons. A higher content of glass microballoons or gas bubbles is necessary if the product is to be used in a small-diameter drillhole, or if the explosive has to be cap-sensitive. The packaged cap-sensitive emulsion explosives in small cartridge diameters have prices approaching those of low grade dynamites.

Emulsion/ANFO Mix Explosives, Heavy ANFO

The bubble-sensitized emulsion blasting agent is used by itself in very wet drillholes, or in drillholes with running water, where ANFO would be unusable because of its high solubility in water. For moderately wet drillholes which can be pumped dry before use, or where the flow of water through the hole is slow, so-called heavy ANFO is used, consisting of a mix of ANFO and emulsion, containing more emulsion the more water there is in the drillholes. Typical heavy ANFO qualities contain either about 40 % (by weight) emulsion, in which case they can be augered into slightly wet drillholes, or 60 % emulsion, in which case the product can be pumped using the same equipment used to pump the neat emulsion. The heavy ANFO explosives in large bulk quantities sell at prices between \$170 and \$190 per ton, the higher price for the higher emulsion content explosives.

Slurry Explosives, Water Gels

The emulsion explosives, because of their competitive prices, have almost entirely taken over the market share previously held by slurry or water-gel explosives. A typical slurry explosive consists of a liquid phase consisting of ammonium nitrate and calcium or sodium nitrate dissolved in water and thickened or gel led by the addition of a gelling agent such as guar gum. Additional AN in the form of prills and a sensitizer such as TNT flakes or grains is mixed into the thickened solution, forming a slurry, of a consistency similar to breakfast porridge, which can be pumped into the drillhole and further thickened by crosslinking of the guar gum to a rubbery consistency which has quite good water resistance although it is somewhat water soluble. The name *water gel explosive* is sometimes used interchangeably with slurry explosives, but more often indicates a waterbased ammonium nitrate explosive in which a water soluble sensitizer such as monomethyl ammonium nitrate (MMAN) is used instead of the TNT. Slurry explosives are generally much more expensive than emulsion explosives because of the high price of the TNT or MMAN sensitizer. The slurry production process is also more costly than that used in making emulsions. Slurry explosives have advantages as carriers for demil explosives or propellants, however, because the demil material can be used as a sensitizer to replace the regular TNT or MMAN sensitizer.

The prices as indicated are much lower than those of new military explosives, which start at perhaps \$800 per short ton for TNT and \$8,000 per ton for Comp. B. It is obvious that it will

be very difficult to persuade a producer or user of commercial explosives to replace any of the standard commercial explosives by TNT at current TNT-prices, and even less at current Comp. B-prices, even if the commercial explosive may have a somewhat lower strength than that of TNT.

3. DEMIL MATERIALS

In this discussion, we will exemplify demil materials of different kinds by some sample compositions, selected to illustrate how the addition of demil materials of different kinds affect the energy and output of typical commercial explosives.

TNT

TNT is the explosive stockpiled in overwhelmingly the largest quantity of all military explosives, and it may be expected to also be available as a demil material in the largest quantities, although there is still some demand for new TNT at world market prices for new TNT, perhaps at a price of \$800 per short ton. It is therefore well worth making considerable efforts to requalify TNT from demilitarized munitions so that it can be sold at these prices. However, the quantities of munitions containing TNT in need of demilitarization are so large, and increase so rapidly because of decreasing available storage space or other reasons, that it is doubtful if the material can be requalified at a sufficiently fast rate.

Composition B

Composition B, consisting of 40 % TNT and 60 % RDX, is the military explosive used in the largest quantities next to TNT. Comp B is a higher density, more energetic explosive than TNT.

Tritonal

Tritonal is a mix of 20 % aluminum in TNT. Because of its low sensitivity, it is used in large deep penetrating bombs and in underwater mines. The special advantage in deep penetrating bombs is its great friction and impact insensitivity, and its, compared to TNT, much increased expansion work or heave energy. This is also why the explosive has found use in underwater mines.

Ammonium perchlorate based large rocket propellant (PropAP)

Ammonium perchlorate is the most oxygen rich oxidizer available in large quantity at a reasonably low price (compared to military explosives prices) and aluminum is the most energy rich, reasonably priced fuel available in large quantity. The combination of these together with a rubbery binder, often hydroxy terminated polybutadiene (HTPB), is the basis of the large booster rocket propellants used, for example, in Minuteman rocket motors.

Single-base gun propellant

The initial use of nitroglycerine in gun propellants was to provide a solvent for nitrocellulose, and a typical single-base gun propellant consists of the main ingredients nitrocellulose (NC) and nitroglycerine (NG) in the proportions 95% NC with 5% NG (neglecting, as done in the calculations in this paper, small but very important ingredients such as graphite which reduces

static electricity, and stabilizers such as diphenylamine which increase storage life. The material has a density of about 1.5 g/cm^3 , and is stored as single- or multi-hole cylindrical grains of a variety of dimensions, long sticks, and leaves.

Double-base gun propellant

The typical double-base propellant consist of about equal parts of NG and NC. As with the single-base propellant in our calculations, we have omitted some other ingredients present in small quantities.

4. CALCULATED REACTION PRODUCTS

Calculations

In the following, the approximate ingredient formulations and reaction products of about 20 different commercial and military explosives, propellants, and mixed commercial/military explosives or propellants are listed. These have been calculated by the TIGERWIN computer code with the BKW equation of state for the reaction products, recently calibrated by Baer and Jones at Sandia National Laboratories. These Sandia-calibrated BKW parameters are referred to as BKWS parameters. The calculation outputs contain a rich harvest of reaction product compositions, not only at the detonation state, but also during the expansion. It would carry this discussion too far to discuss all these. We have selected to present here the reaction product compositions for all these explosives at the ideal detonation state (the Chapman-Jouguet or CJ detonation state), assuming complete chemical reaction to a mix of reaction products which are in chemical equilibrium with each other. This is a limiting case, which contains a minimum of toxic or otherwise unwanted reaction products such as CO, NO, NO₂, H₂, CH₄, and NH₃. It is approximately correct for explosives detonating in a large (8 - 15 inch diameter) drillhole in rock, when the ingredients are intimately mixed together. In smaller diameter drillholes, and when some of the ingredients are present in large grain size, the percentages of these unwanted reaction products increase rapidly. Also, as the reaction products cool from the ideal detonation state as a result of expansion work done, the temperature of the initial reaction products may be so low that little mix reaction will take place with the reaction products from any late burning of large grained ingredients. This will produce greater amounts of unwanted reaction products than if all ingredients reacted together.

Discussion of results

As can be seen from Table 1, all of the military demil energetic materials, because they are oxygen deficient, generate considerable quantities of CO, NH₃, CH₄, and H₂ under detonation conditions by themselves. The two containing aluminum, namely Tritonal and the AP-based large rocket propellant (here called PropAP), also generate dust in the form of alumina (Al₂O₃), and solid carbon, soot. Soot is also created by both TNT and Composition B. PropAP also generates hydrochloric acid, HCl.

In contrast, as can be seen from Table 2, the amounts of the unwanted reaction products CO, NH₃, H₂, and CH₄ are much lower for the most common commercial explosives. Close to oxygen balance, ANFO appears to have a small but calculable amount of NO. Especially

favorable is the aluminum based slurry, which has almost none of the unwanted gaseous reaction products, although it does generate some alumina dust.

By way of example, Table 3 shows the three major types of commercial explosives ANFO, Emulsion, and the emulsion/ANFO mix often called EmulAN, each of which is mixed with 25 % and 5 % TNT. Surprisingly, when the TNT-content is reduced by a factor of 5, the amounts of unwanted fumes is reduced by less than a factor of 5. Since the three commercial explosives are nearly oxygen balanced by themselves, the addition of the oxygen deficient demil materials generates these rather large quantities of unwanted fumes.

Table 4 shows the effect of adding 25 weight % of the six sample demil materials to pure ammonium nitrate (AN), i. e. AN without any fuel oil. We can see that the contents of unwanted fumes are considerably reduced when the strongly oxygen deficient TNT, Tritonal, and PropAP are added to AN. In contrast to this, when the less oxygen deficient CompB and either of the single and double base propellants are added to AN, considerable amounts of the particularly noxious gas NO is generated.

Table 5 shows the effect of adding 25 weight % of the same six demil materials to ANFO, which is oxygen balanced by itself. The smallest amounts of unwanted reaction products is found for ANFO with 25 % Double base propellant (PropDB).

General trends

The discussion indicates that there is no single commercial explosive uniquely suited to take large additions of demil material without modification. Each one of the sample demil materials will require a careful analysis and consideration as to which type of commercial explosive is the best carrier, and what modifications need to be made to the joint formulation for best results. From the environmental viewpoint, *however, these calculations show clearly the importance of seeking a mix that is completely oxygen balanced.* The percentage of demil material to be added is probably also strongly influenced by the requirement that *the resulting material must be a non cap-sensitive blasting agent rather than a Class A explosive.*

In the following section, some tentative compositions are proposed. These are, however, only by way of illustration to the reasoning in this paper.

Table 1. Composition and reaction products of some sample demil energetic materials

Property \ Name	TNT	CompB	Tritonal	PropAP	PropSB	PropDB
Ingredients (weight %)						
TNT	100	40	80			
RDX		60				
Aluminum			20	25		
Ammonium perchlorate				55		
Plastic binder HTPB				20		
Nitrocellulose 13					95	50
Nitroglycerin					5	50
Reaction products (CJ-det) (Moles/kg explosive, prop.)						
'CO ₂	6.36	5.35	0.71	0.19	8.15	10.09
'CO	4.7	4.58	6.06	1.95	9.06	5.18
'N ₂	6.08	9.95	4.71	1.3	4.43	5.54
'NH ₃	1.04	1.59	1.14	2.09	0.86	0.3
'H ₂ O	4.77	4.92	1.86	2.14	6.16	8.99
'H ₂	0.5	0.54	1.89	2.74	0.89	0.56
'CH ₄	1.04	0.69	1.5	5.95	0.88	0.02
'NO						
'NO ₂						
'Al ₂ O ₃			3.71	4.63		
Solid C	16.61	6.52	16.04	6.31		
'HCl				0.35		

Table 1.
Composition and reaction products of some sample demil energetic materials

Table 2. Composition and reaction products of some commercial explosives

Property / Name	ANFO	Emu	EmuAN	TNT-slu	Al-slu
Ingredients (weight %)					
AN	94	76	86.8	65	75
CN				15	
Fuel oil	6	6	6		
Ethylene glycol					5
Guar gum				2	2
Emulsifier		2	0.8		
Water		16	6.4	15	11
TNT or MMAN				20	
Aluminum					7
Reaction products (CJ-det) (Moles /kg explosive)					
'CO ₂	3.74	3.79	3.57	6.02	2.38
'CO	0.19	0.92	0.78	0.01	0.01
'N ₂	11.77	8.74	10.54	8.2	9.31
'NH ₃	0.01	1.51	0.59		
'H ₂ O	27.63	28.69	28.01	22.58	27.31
'H ₂	0.2	1.47	1.03		0.02
'CH ₄		0.41	0.02		
'NO	0.03				
'NO ₂					
'Al ₂ O ₃					1.3
'Solid C					
'CaCO ₃				0.91	

Table 2. Composition and reaction products of some commercial explosives

Table 3. Composition and reaction products of commercial explosives mixed with 25% TNT.

Property / Name	ANFO + 25% TNT	ANFO + 5 % TNT	Emu + 25 % TNT	Emu + 5 % TNT	EmuAN +25 % TNT	EmuAN + 5 % TNT
Ingredients (weight %)						
AN	70.5	89.3	57	72.2	65.1	82.46
Fuel oil	4.5	5.7	4.5	5.7	4.5	5.7
Emulsifier			1.5	1.9	0.6	0.76
Water			12	15.2	4.8	6.08
TNT	25	5	25	5	25	5
Reaction products (CJ-det) (Moles /kg explosive)						
'CO ₂	4.18	3.86	6.05	4.33	5.45	4.08
'CO	6.32	1.64	2.81	1.29	3.84	1.46
'N ₂	10.09	11.41	7.75	8.5	8.86	10.07
'NH ₃	0.74	0.16	2.05	1.69	1.84	1.13
'H ₂ O	18.02	25.32	18.32	26.51	17.54	25.46
'H ₂	4.09	1.6	1.55	1.6	2.01	1.55
'CH ₄	0.21		2.06	0.7	1.19	0.13
'NO						
'NO ₂						
'Al ₂ O ₃						
Solid C						

Table 3. Composition and reaction products of commercial explosives mixed with 25% TNT.

Table 4. Composition and reaction products of 75 weight % ammonium nitrate (AN) mixed with 25 weight % of some sample demil energetic materials

Property \ Name	AN + 25% TNT	AN + 25% CompB	AN +25% Tritonal	AN + 25% PropAP	AN + 25% PropSB	AN + 25% PropDB
Ingredients (weight %)						
Ammonium nitrate	75	75	75	75	75	75
TNT	25	10	20			
RDX		15				
Aluminum			5	6.25		
Ammonium perchlorate				13.75		
Plastic binder HTPB				5		
Nitrocellulose 13					23.75	12.5
Nitroglycerin					1.25	12.5
Reaction products (CJ-det) (Moles/kg explosive, prop.)						
'CO ₂	6.2	5.04	4.46	2.92	5.17	4.29
'CO	1.45	1.17	1.65	0.72	0.01	
'N ₂	10.99	11.83	10.63	9.9	10.39	10.59
'NH ₃	0.05		0.06	0.04		
'H ₂ O	20.72	21.84	19.86	22.63	21.92	21.72
'H ₂	0.65	0.02	0.94	0.71	0.01	
'CH ₄						
'NO	0.03	0.44	0.06	0.07	0.4	0.39
'NO ₂						
'Al ₂ O ₃				1.15		
'HCl				0.8		

Table 4. Composition and reaction products of 75 weight % ammonium nitrate (AN) mixed with 25 weight % of some sample demil energetic materials

Table 5. Composition and reaction products of 75 weight % ANFO mixed with 25 weight % of some sample demil energetic materials

Property \ Name	ANFO + 25% TNT	ANFO + 25% CompB	ANFO + 25% Tritonal	ANFO + 25% PropAP	ANFO + 25% PropSB	ANFO + 25% PropDB
Ingredients (weight %)						
Ammonium nitrate	70.5	70.5	70.5	70.5	70.5	70.5
Fuel oil	4.5	4.5	4.5	4.5	4.5	4.5
TNT	25	10	20			
RDX		15				
Aluminum			5	6.25		
Ammonium perchlorate				13.75		
Plastic binder HTPB				5		
Nitrocellulose 13					23.75	12.5
Nitroglycerin					1.25	12.5
Reaction products (CJ-det) (Moles/kg explosive, prop.)						
'CO ₂	4.18	4.17	2.92	2.18	5.2	5.59
'CO	6.32	3.93	6.07	4.38	3.03	1.8
'N ₂	10.09	11.26	9.71	8.94	9.91	10.18
'NH ₃	0.74	0.46	0.84	0.89	0.23	0.09
'H ₂ O	18.02	20.54	16.68	18.65	21.96	22.82
'H ₂	4.09	2.75	4.8	5.19	1.82	1.01
'CH ₄	0.21	0.03	0.18	0.14	0.01	
'NO						0.01
'NO ₂						
'Al ₂ O ₃			0.93	1.16		
'HCl				1.08		

Table 5. Composition and reaction products of 75 weight % ANFO mixed with 25 weight % of some sample demil energetic materials

5. PROPOSED ENVIRONMENTALLY ACCEPTABLE FORMULATIONS

The calculations give some general guidance as to the direction in which to seek the optimal commercial/demil material mix. The following are some tentative recommendations.

TNT, Composition B, and Tritonal in ANFO

These three demil materials, which are rather friction insensitive, are all castable. By melting them and mixing the melt with ammonium nitrate prills in a proportion that is oxygen balanced (which means a different addition percentage for each demil material), an explosive is produced which is oxygen balanced and therefore can be mixed with ANFO in all proportions while still maintaining oxygen balance. Another advantage is that the melt-mix with the AN prills becomes very intimate. The proportion to use for rock blasting is then determined by the condition that the material shall be a blasting agent, i.e. non cap-sensitive. This proportion has to be experimentally determined for each individual demil material.

Ammonium perchlorate/aluminum large rocket propellant, single base, and double base propellant in slurry explosives

The AP/Al/HTPB rocket propellant is perhaps the most difficult for which to propose a suitable commercial explosives carrier. In a longer time perspective, it would seem that a material as expensive as AP will ultimately have to be recovered, purified, and re-qualified for use in other booster rocket propellants, or in new composite explosives formulations that build on AP as an oxidizer. In the meantime, use a low percentage aluminized slurry as the carrier. In the author's opinion, the best result from an environmental point of view will be found when the mix is oxygen balanced, and when the propellant is sufficiently finely divided so that the burning of each grain is completed before the pressure in the drill hole drops below a level of, say, 1000 bar. This condition would probably exclude the use of large pieces (several inches in diameter) of the propellant, but the optimal size of the propellant grains will have to be experimentally verified.

The single-base and double-base gun propellants, which are much less oxygen deficient than the other demil materials discussed here, can preferably be used as an ingredient in a slurry explosive, where the conventional sensitizer/fuel, be it TNT, MMAN, or aluminum, is partly replaced by the propellant. Grinding these rather friction sensitive demil materials to the required grain size is best done under water, or with added water. By adjusting the water content of the base slurry, the water added to the propellant for safety in the grinding operation does not have to be removed, but can go into the total formulation. This also reduces the need for treating the process waste water, which may contain small percentages of nitroglycerin.

For all these formulations, it is obvious that large diameter drillholes will provide the longest time for thermal equilibrium and complete combustion of the added demil materials. Large blasts with large diameter drillholes therefore appears to be the best place to demonstrate the benefits outlined in this paper.

The use of these formulations in packaged form, using the standard plastic 25 lb bags fitting

in drillholes of 4 to 10 inch diameter, will avoid a host of safety questions that would come up before the products could be qualified for use in bulk, especially with respect to the safety of pumping such compositions with the pumps normally used for slurry or emulsion explosives. A possible exception might be ANFO made with small additive percentages of the proposed TNT-impregnated AN prills. ANFO is generally augered from a bulk truck into drillholes using augers of the type commonly used in grain elevators. Although TNT is an explosive and therefore must be treated with special respect, it is also one of the most friction and impact insensitive of explosives. Therefore, it might be possible to devise safety measures such that ANFO containing small additive percentages of TNT-impregnated AN prills could be qualified for use in such equipment in bulk.

6. VERIFICATION PROGRAM

The results of the theoretical study presented in this paper require verification. The positive environmental impact of a program of demilitarization along the lines proposed here is very considerable in view of the very large quantities of demil materials that need to be dealt with during the next few years. The proposed use of oxygen balanced compositions of commercial explosives containing demil materials may provide very large environmental gains when compared to the present techniques of burning or detonating in the open air which now consumes most of the demil material coming out of the stockpile, or to the present crude methods of mixing demil materials into conventional explosives without considering the oxygen balance.

A verification program would start with laboratory scale detonation experiments of 1-3 kg charges of oxygen balanced compositions developed from the thoughts presented in this paper. The detonation experiments should be accompanied by friction and drop-weight impact tests to ascertain the safety of the compositions proposed. Finally, a technique for routine sampling the reaction products from large scale test blasts in real large diameter drillhole rounds must be developed. Work in this direction is already under way at the Research Center for Energetic Materials.

7. CONCLUSIONS

This paper recommends techniques for developing oxygen balanced compositions of mining explosives containing demil energetic materials. The formulations developed have to be considered from the environmental as well as from a safety point of view. A development and testing program is proposed for verifying the findings.